PCT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C01B 17/02, 17/04	A1	(11) International Publication Number: WO 95/06616
		(43) International Publication Date: 9 March 1995 (09.03.95)

(21) International Application Number: PCT/CA94/00481

(22) International Filing Date: 31 August 1994 (31.08.94)

(30) Priority Data:
9318122.0   1 September 1993 (01.09.93)   GB
9403709.0   25 February 1994 (25.02.94)   GB

(71) Applicants (for all designated States except US): APOLLO ENVIRONMENTAL SYSTEMS CORP. [CA/CA]; Suite 119, Lansing Square, Willowdale, Ontario M2J 5A2 (CA). PROCOR SULPHUR SERVICES INC. [CA/CA]; 310 Southport Atrium, 10333 Southport Road S.W., Calgary, Alberta T2W 3X6 (CA).

(72) Inventors; and
(75) Inventors/Applicants (for US only): ELLENOR, David, Todd, R. [CA/CA]; 104 Blantyre Avenue, Scarborough, Ontario M1N 2R5 (CA). SMITH, James, W. [CA/CA]; 33 Airdrie Road, Toronto, Ontario M4G 1L8 (CA). HARBINSON, John, H. [CA/CA]; 44 Macklingate Court, Scarborough, Ontario M1V 1A1 (CA). DE PAOLI, Sergio [CA/CA]; 468 Parkridge Rise, Calgary, Alberta T2J 5C3 (CA).

(74) Agent: STEWART, Michael, L.; Suite 701, 330 University Avenue, Toronto, Ontario M5G 1R7 (CA).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).

Published
With international search report.

(54) Title: LIQUID SULFUR DEGASSING

(57) Abstract

Liquid sulfur is degassed to remove hydrogen sulfide and hydrogen polysulfides in rapid and efficient manner using a shroud and impeller combination which distributes a stripping gas, which may be steam or air, as small bubbles in the liquid sulfur in the presence of a strong Bronsted-Lowry base catalyst and provides parameters which provide rapid and efficient mass transfer. Such degassing may be combined with Claus plant tail gas clean up, by using the tail gas as the stripping gas. In addition, Claus plant tail gas clean up may be effected in liquid sulfur.
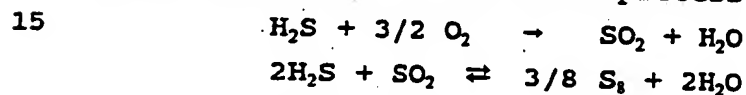
TITLE OF INVENTION
LIQUID SULFUR DEGASSING

FIELD OF INVENTION
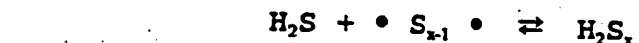
5   The present invention is directed to the removal of hydrogen sulfide and hydrogen polysulfides from liquid sulfur in rapid and efficient manner.

BACKGROUND OF THE INVENTION

Hydrogen sulfide is a product which may be recovered
10   during the production of natural gas, refining operations, or as a byproduct of a number of industrial operations.   In many cases the hydrogen sulfide is converted to elemental sulfur by the Claus process. The basic chemistry of the Claus process is as follows:

15       $$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$$
$$2H_2S + SO_2 \rightleftharpoons 3/8\ S_8 + 2H_2O$$

Hydrogen sulfide is, to a limited degree, soluble in liquid sulfur. This dissolved hydrogen sulfide may react with the sulfur diradical chain species to form hydrogen
20   polysulfides, as follows:

$$H_2S + \bullet S_{x-1} \bullet \rightleftharpoons H_2S_x$$

Liquid sulfur produced by the Claus process may contain from 50 to 550 ppmw of hydrogen sulfide species. The hydrogen sulfide and hydrogen polysulfides slowly
25   reach an equilibrium in the liquid sulfur which is substantially influenced by temperature. Over time, the hydrogen sulfide diffuses out of the liquid sulfur, or in cases where the sulfur has been solidified, out of the solid product. Under ambient conditions, it can take
30   weeks for the hydrogen polysulfides to decompose to sulfur and hydrogen sulfide. The release of these hydrogen sulfide emissions may create a variety of nuisance, environmental and safety concerns, if not properly controlled. Examples of such concerns are:
35   -   hydrogen sulfide concentrations can build up to lethal and explosive limits in the

SUBSTITUTE SHEET

2

headspace when liquid or formed sulfur is
stored or shipped within an enclosed space.

–   low levels of hydrogen sulfide emissions
    coming off sulfur storage facilities can be
5   environmentally objectionable due to the low
    odour threshold of only 0.003 to 0.02 ppmw
    (ref. 1).

–   liquid sulfur is often processed into a solid
    formed product for transportation purposes,
10 and very often hydrogen sulfide is released to
    the atmosphere during such forming, storage
    and transportation operations.

Over the years many systems have been designed to
remove hydrogen sulfide and hydrogen polysulfides from
15 liquid sulfur. A review of the prior art reveals that
some systems favour the use of reagents or catalysts to
effect the removal, while others use air or gas and
agitation of the liquid sulfur to promote the release of
hydrogen sulfide. It has been found that the use of some
20 catalysts or reagents, such as urea, may assist in the
removal of hydrogen sulfide, but it is believed that the
friability of formed sulfur product may be impacted
negatively by these compounds. Many systems use large
vessels to hold the liquid sulfur and sparge air or an
25 inert gas through the liquid sulfur to provide
circulation and a carrier gas to remove the hydrogen
sulfide from the liquid sulfur. The residence time for
such processes generally ranges from several hours to, in
some cases, several days. The inert gas may consist of
30 steam or nitrogen, and is generally used to reduce the
risk of fire or explosion. In addition, such prior art
systems often result in residual hydrogen sulfide and
hydrogen polysulfide levels of at least about 50 ppmw.

The prior art als comprises mechanical systems with
35 air or gas sparging which decrease the residence time of
the liquid sulfur by increasing the degree of agitation.

3

U.S. Patent No. 4,612,020 describes a system where liquid sulfur is sprayed into two or more chambers, which are joined in series, and the liberated hydrogen sulfide is scavenged from the head space by an inert gas, such as
5   nitrogen.   The residence time for the liquid sulfur as noted in this patent varies from 12 to 32 hours.   Such residence times require extremely large degassing vessels to be employed.   This residence time can be decreased to about 7 hours by using hetrocyclic amine catalysts.   The
10   present invention employs a new approach to the degassing of liquid sulfur, which in turn facilitates dramatically reduced residence times.   While reference was made earlier to liquid sulfur produced by a Claus plant, the present invention may be applied to liquid sulfur
15   produced by other processes as well.

        Searches of the prior art have revealed several patents relating to the removal of hydrogen sulfide from liquid sulfur and the use of various catalyst materials in such procedures, as described above.   As a result of
20   such searches, the applicants are aware of the following references:

        USP 3,364,655   USP 3,447,903   USP 3,807,141
        USP 4,131,439   USP 4,612,020   USP 4,755,372
        USP 4,844,720   USP 4,849,204   USP 5,030,438
25   USP 5,080,695   GB 1,067,815   CA 964,040

                    SUMMARY OF INVENTION

        The present invention provides an improved procedure for the removal of hydrogen sulfide and hydrogen polysulfides from liquid sulfur which enables the normal
30   degassing time to be reduced from hours or days to minutes while achieving residual H_2S and H_2S_x levels below 5 ppmw.   The procedure of the invention may employ the gas-liquid contactor generally described in USP 5,174,973 for the removal of a gaseous component from a gas stream
35   in an aqueous system using parameters developed for

4

aqueous systems, but modified for the removal of hydrogen
sulfide and hydrogen polysulfides from liquid sulfur.

In one aspect of the present invention, there is
provided a method of removing hydrogen sulfide and
5   hydrogen polysulfides from liquid sulfur, which comprises
providing a rotary impeller comprising a plurality of
blades at a submerged location in the liquid sulfur
surrounded by a shroud through which are formed a
plurality of openings, feeding a stripping gas for
10   hydrogen sulfide to the submerged location while
providing a Bronsted-Lowry base catalyst for the
conversion of hydrogen polysulfides to hydrogen sulfide
thereat, rotating the impeller about a substantially
vertical axis at a speed sufficient to draw liquid sulfur
15   into the interior of the shroud and to distribute the
stripping gas as bubbles in the liquid sulfur to the
interior of the shroud and to form a gas-liquid mixture
of bubbles of the gas in the liquid sulfur contained
within the shroud, flowing the gas-liquid mixture from
20   within the interior of shroud through and in contact with
the openings to external of the shroud, and removing the
stripping gas from the liquid sulfur.

In one preferred aspect, the present invention
provides a method of removing hydrogen sulfide and
25   hydrogen polysulfides from liquid sulfur, which comprises
a plurality of steps. A rotary impeller comprising a
plurality of blades is provided at a submerged location
in the liquid sulfur surrounded by a shroud through which
are formed a plurality of openings. A stripping gas for
30   stripping hydrogen sulfide from the liquid sulfur is fed
to the submerged location. The impeller is rotated about
a substantially vertical axis at a speed corresponding to
a blade tip velocity (v_i) of at least about 150 in/sec (at
least about 4 m/s), preferably at least about 350 in/sec
35   (at least about 9 m/s), so as to draw liquid sulfur into
the interior of the shroud and to generate sufficient

shear f rces between the impeller and the plurality of openings in the shroud to distribute the stripping gas as bubbles in the liquid sulfur to the interior of the shroud and to effect intimate contact of the stripping 5 gas and the liquid sulfur at the submerged location so as to form a gas-liquid mixture of bubbles of the stripping gas in the liquid sulfur contained within the shroud while effecting shearing of the gas-liquid mixture within the shroud. The gas-liquid mixture is flowed from within 10 the interior of the shroud through and in contact with the openings to external of the shroud at a gas velocity index (GVI) of at least about 4 per second per opening in the shroud, preferably at least about 18 per second per opening, so as to effect further shearing of the gas- 15 liquid mixture and further intimate contact of the stripping gas and the liquid sulfur.

The gas velocity index (GVI) is determined by the expression:

$$GVI = \frac{QP}{4nA^2}$$

20 where Q is the volumetric flow rate of gas into the impeller (m^3/s), n is the number of openings in the shroud, A is the area of the opening (m^2) and P is th length of the perimeter of the opening (m).

The method is carried out:
25 (a) at an Effective Shear Index (ESI) value of about 1 to about 6000 as determined by the relationship:

$$ESI = \frac{GVI}{V_i} X \frac{(D_s - D_i)}{2} X100$$

where D_s is inside diameter (m) of the shroud and D_i is the utside diameter (m) of the impeller,
30 (b) at a Shear Effectiveness Index (SEI) value of about 1 to about 25 as determined by the relationship:

$$SEI = \frac{Q}{\pi h D_i V_i} X 100$$

where h is the height of the impeller (m), and

(c) at a Density Index (DI) value of about 1 to about 8 as determined by the relationship:

$$DI = \frac{Q}{Q_i} \left[\frac{\rho_L - \rho_g}{\rho_{H2O} - \rho_{air}} \right]$$

5

where Q_i is the self-induction flow rate of air into water (m^3/s), ρ_L is the density of the liquid sulfur (kg/m^3), ρ_g is the density of the gas (kg/m^3), ρ_{H2O} is the density of water (kg/m^3) and ρ_{air} is the density of air (kg/m^3).

10   The accelerated and efficient degassing process provided herein enables equipment size to be significantly decreased for a given mass throughput and avoids the necessity and expense of constructing large holding tanks or storage pits to accommodate the

15   traditional longer degassing residence times. Since small vessels suffice to give the needed residence time, the equipment necessary for effecting the present invention may be very compact in relation to its production rate, and requires a small capital investment

20   and possesses low operating costs.

The process of the invention may be used to effect hydrogen sulfide and hydrogen polysulfide degassing of individual batches of liquid sulfur in a treatment vessel, or, alternatively, to effect degassing of a

25   continuous feed of liquid sulfur to a treatment vessel or a series of treatment vessels.

In the process of the invention, the removal of hydrogen sulfide from the liquid sulfur produced by the stripping gas shifts the equilibrium of the equation:

30       $H_2S + S_{x-1} \rightleftharpoons H_2S_x$

7

to the left, causing decomposition of hydrogen polysulfides. This reaction is catalyzed, as outlined below, by the presence of a Bronsted-Lowry base, with stronger Bronsted-Lowry bases causing a greater catalytic

5 effect. Such Bronsted-Lowry base may be provided by utilizing steam as the stripping gas.

In general, the hydrogen sulfide and hydrogen polysulfide stripping operation is effected in the presence of a strong Bronsted-Lowry base catalyst soluble

10 in the liquid sulfur. Such catalyst may be provided to the interior of the shroud and impeller combination in any convenient manner. For example, the catalyst may be introduced into the liquid sulfur flowing into a treatment vessel and/or may be introduced into the

15 vessel, so as to be transported to the submerged location by the general circulation of liquid sulfur. Alternatively, the catalyst may be transported by any other convenient manner to the liquid sulfur at the submerged location. For example, the catalyst may be

20 injected into the stripping gas or may be injected directly into the vortex of liquid sulfur formed inside the shroud. In this latter procedure, the difference in temperature generally existing between the stripping gas and the liquid sulfur may promote stripping of hydrogen

25 sulfide in the presence of the catalyst. When the stripping operation is carried out in this way, a temperature differential between the cooler stripping gas and liquid sulfur of at least about 20°C is maintained. In general, the stripping gas may have a temperature of

30 at least about 20°C and preferably less than about 100°C.

During the course of a series of experiments in two different sulfur processing plants to determine the efficacy of an impeller and shroud combination for the agitation of liquid sulfur and the stripping of hydrogen

35 sulfide, it was observed that the addition of steam in one of the plants to the stripping gas stream which was

8

intimately and vigorously contacted with the sulfur facilitated rapid decreases in the concentration of hydrogen polysulfides. Two different reaction vessels were used in the tests in each of the two sulfur plants,
5 but each reaction vessel was designed in the manner illustrated in Figure 1 and described below. In both series of tests conducted at sulfur plants A and B, when air alone was passed through the contacting system, the free hydrogen sulfide was stripped from the liquid sulfur
10 with a half-life of approximately one minute or less, and the rate of reaction for the removal of the hydrogen polysulfides ranged from a half life of 40 to 60 minutes. However, when steam from plant A was contacted with the liquid sulfur, the rate of reaction for the removal of
15 the hydrogen polysulfides increased to a half-life of less than 6 minutes. Subsequent experiments using different proportions of steam to air resulted in a half-life of about 9 to 15 minutes. In all cases, where steam was employed, the hydrogen sulfide was rapidly stripped
20 from the liquid sulfur, with an estimated half-life of 60 seconds or less.

When this series of experiments was repeated under more readily controlled conditions at sulfur plant B, using a smaller reactor system, it was discovered that
25 the steam did not have the same effect as that used in sulfur plant A. In fact, the effect of steam appeared t be relatively minor, and once again, the half-lives for the decomposition of hydrogen polysulfides were in the order of 30 to 50 minutes, depending on experimental
30 conditions. However, the period represents a considerable improvement over the 3 to 6 hours observed using an inert gas for the stripping.

A careful investigation lead to the finding that certain organic amines were used in the treatment of
35 boiler water at gas plant A, but were n t used at gas plant B, leading to the surprising and unexpected

discovery that these additives, although present in only
trace amounts in the steam, increased the reaction rate
to half lives of 1 minute of less, in very great contrast
to prior art, and even to our earlier results.

5   Almost any amine, including ammonia, promotes the
rapid conversion of hydrogen polysulfides to hydrogen
sulfide, which then are readily and efficaciously removed
by the contactor system provided herein. It is observed
that such amine materials have been used and are recorded

10   in prior art, but the half lives reported for the
degassing process have been significantly longer than
those noted herein. This surprising and unexpected
discovery that a combination of vigorous agitation and
stripping, such as with a contactor operating under the

15   conditions described herein, with the very high mass
transfer rates, together with the addition of trace
amounts of Bronsted-Lowry bases enables a process to be
designed which will degas liquid sulfur much more quickly
and with reduced equipment size compared to that of

20   competing systems, because the residence time for the
sulfur can be significantly shortened.

       It was observed during the series of experiments at
sulfur plant B that steam, in effect, played a relatively
minor role in the change in the removal of the hydrogen

25   polysulfides over that of air. The addition of a mixture
of morpholine and cyclohexylamine resulted in half lives
for the decomposition of hydrogen polysulfide in the
order of 25 seconds or less. An analysis by FTIR showed
the catalyst, water and volatile impurities also are

30   rapidly and nearly completely removed, resulting in a
very pure sulfur product.

                    BRIEF DESCRIPTION OF DRAWINGS

       Figure 1 is a schematic perspective view, with parts
broken away, of a liquid sulfur degassing device,

35   provided in accordance with one embodiment of the
invention;

Figure 2 is a FTIR spectrum of liquid sulfur showing residual concentrations of H_2S and H_2S_x prior to treatment;

Figure 3 shows in graphical manner the decrease in
5   concentration of H_2S and H_2S_x in a pilot plant contactor operating in accordance with one embodiment of the present invention using an air stripping gas in the absence of catalyst;

Figure 4 shows the concentration of hydrogen sulfide
10   with time for the effluent from a pilot scale contactor operating in accordance with one embodiment of the present invention using an air stripping gas in the absence of a catalyst;

Figure 5 illustrates the effect of catalyst on the
15   rate of decrease in concentration of H_2S_x in a bench-scale contactor operating in accordance with one embodiment of the invention using an air stripping gas;

Figure 6 shows FTIR spectrum of liquid sulfur for H_2S and H_2S_x with time post-catalyst injection in the
20   results shown in Figure 5;

Figure 7 contains a comparison of FTIR spectra before and after catalyst addition;

Figure 8 contains a comparison of FTIR spectra for feed and product samples for a steady state flow-through
25   test;

Figure 9 is a graphic representation of the H_2S_x half-life vs catalyst concentration in a pilot-scale contactor with continuous flow-through tests;

Figure 10 contains a comparison of FTIR spectra for
30   an initial feed sample and final degassed sample for a liquid sulfur degassed according to the present invention and having residual H_2S and H_2S_x concentrations below 2 ppmw, and

Figure 11 is a graphical representation of the
35   effect of catalyst concentration on the quantity of SO_2

in the off-gas from a pilot plant contactor using an air stripping gas.

GENERAL DESCRIPTION OF INVENTION

The present invention is concerned with a procedure
5 for removing hydrogen sulfide and hydrogen polysulfides from liquid sulfur in a rapid and efficient manner t result in low residual hydrogen sulfide and hydrogen polysulfide levels. The liquid sulfur processed herein may be that produced by a Claus plant converting hydrogen
10 sulfide recovered from oil refining or sour gas to elemental sulfur. However, liquid sulfur containing dissolved hydrogen sulfide and hydrogen polysulfides from any other source may be treated using the procedure of the present invention.
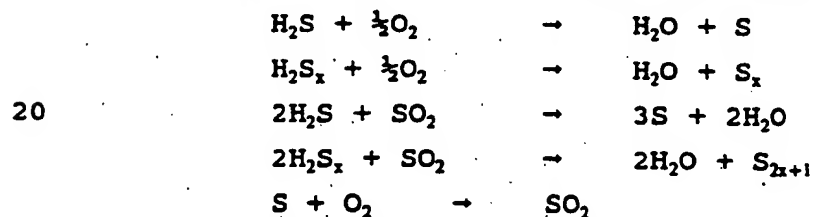
15 Accordingly, the present invention provides a method of removing hydrogen sulfide and hydrogen polysulfides from liquid sulfur, comprising a plurality of steps. The method of the invention is carried out at a temperature at which sulfur is in a molten state. At temperatures
20 above about 160°C, liquid sulfur becomes more viscous. The preferred temperature range for a system as described herein is about 120°C to about 160°C, more specifically, about 125°C to 155°C. The proportion of hydrogen polysulfides to hydrogen sulfide also increases with
25 increases in temperature, and, therefore, it is preferable to degas liquid sulfur within the temperature ranges noted above.

A rotary impeller comprising a plurality of blades is provided at a submerged location in the liquid sulfur
30 surrounded by a shroud through which are formed a plurality of openings, within a range of impeller to shroud diameter ratios as discussed below.

A stripping gas for hydrogen sulfide is fed to a submerged locati n in the liquid sulfur within the
35 shr ud. The stripping gas may comprise steam and removes from the reaction vessel hydrogen sulfide released from

12

the liquid sulfur in the stripping operation. An amine catalyst preferably is utilized in conjunction with the steam, provided in any convenient manner in the liquid sulfur within the shroud. An oxidizing gas also may be
5   employed in the stripping gas. When such oxidizing gas is used, the oxidizing gas may be oxygen or sulfur dioxide, generally transported in an inert carrier gas, such as carbon dioxide or nitrogen or in steam. An amine catalyst preferably is used in conjunction with the
10   oxidizing gas.

A plurality of simultaneous reactions take place in the liquid sulfur resulting in decomposition of hydrogen polysulfides to hydrogen sulfide and stripping of hydrogen sulfide or conversion of hydrogen sulfide to
15   sulfur. Some of the reactions which may take place, depending on the nature of the stripping gas employed may be designated by the following equations:

$$H_2S + \tfrac{1}{2}O_2 \rightarrow H_2O + S$$
$$H_2S_x + \tfrac{1}{2}O_2 \rightarrow H_2O + S_x$$
20
$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$
$$2H_2S_x + SO_2 \rightarrow 2H_2O + S_{2x+1}$$
$$S + O_2 \rightarrow SO_2$$

The stripping gas which is passed through the liquid sulfur should comprise sufficient volume so as to remove
25   the hydrogen sulfide released from the liquid sulfur. It is possible to use Claus process tail gas as the stripping gas since this gas contains nitrogen, water, hydrogen sulfide, sulfur dioxide, carbon dioxide and other constituents. As noted below, the use of a Claus
30   process tail gas stream may result in simultaneous sulfur degassing and Claus plant tail gas clean up.

The catalyst employed herein may be any of the components known to assist the decomposition of hydrogen polysulfides to hydr gen sulfide and sulfur. In general,
35   the catalyst is a Bronsted-Lowry base having a pK_b value of less than about 10, preferably less than about 6.

Added catalyst materials in general are Bronsted-Lowry bases soluble in liquid sulfur, so as to promote the decomposition of the hydrogen polysulfides. Such materials preferably are sufficiently volatile to permit their stripping from the degassed liquid sulfur. Specific examples of such added catalyst materials include volatile aliphatic, cyclic and heterocyclic amines sparingly soluble in the liquid sulfur, as well as ammonia. Such catalysts are preferably organic amines, such as cyclohexylamine and morpholine. Only small quantities of added catalyst are needed, generally in the low parts per million range, generally about 10 ppbw to about 10 ppmw relative to the weight of sulfur, preferably about 1 to about 5 ppmw.

The amine catalysts used herein also catalyze conversion of hydrogen sulfide to sulfur in the presence of sulfur dioxide, so that, when a Claus plant effluent or tail gas stream is utilized as the stripping gas for removal of hydrogen sulfide from the liquid sulfur, the presence of the amine enables Claus plant tail gas clean up and liquid sulfur degassing to be effected in a single step with a single catalyst species.

Such degassing operation in the presence of the amine catalyst and sulfur dioxide in the Claus plant tail gas stream may result in almost complete elimination of hydrogen sulfide from the Claus plant tail gas and fr m liquid sulfur degassing, leaving a gaseous effluent stream free from hydrogen sulfide emissions. In addition to its presence in a Claus plant tail gas stream, the sulfur dioxide employed in this procedure may be provided by burning elemental sulfur or as a slip stream from the Claus plant H_2S burner. It may be preferred to provide a stoichiometric excess of sulfur dioxide to ensure that all hydrogen sulfide, whether in the Claus plant tail gas stream or in the liquid sulfur, is converted to sulfur, to provide a effluent stream which may contain residual

14

sulfur dioxide. Some oxygen may be added to the tail gas stream to effect sulfur dioxide formation _in situ_ in the sulfur and reaction with hydrogen sulfide and/or hydrogen polysulfides to sulfur and water.

5   The ability to effect complete conversion f hydrogen sulfide to sulfur in the presence of liquid sulfur enables there to be provided, in accordance with another aspect of the invention, a Claus plant tail gas clean up procedure in which the hydrogen sulfide content

10   thereof is converted to sulfur by reaction with sulfur dioxide in liquid sulfur, irrespective of the degassing of the liquid sulfur to remove hydrogen sulfide and hydrogen polysulfides therefrom, using the shroud and impeller combination described herein under the process

15   conditions described.

Accordingly, in another aspect of the present invention, there is provided a method for the processing of a hydrogen sulfide- and sulfur dioxide-containing gas stream to remove at least one of the components

20   therefrom, which comprises providing a rotary impeller comprising a plurality of blades at a submerged location in the liquid sulfur surrounded by a shroud through which are formed a plurality of openings, feeding the gas stream to the submerged location, rotating the impeller

25   about a substantially vertical axis at a speed sufficient to draw liquid sulfur into the interior of the shroud and to distribute the gas stream as bubbles in the liquid sulfur to the interior of the shroud and to form a gas-liquid mixture of bubbles of the gas stream in the liquid

30   sulfur contained within the shroud, and flowing the gas-liquid mixture from within the interior of the shroud through and in contact with the openings to external of the shroud, thereby to effect reaction between hydrogen sulfide and sulfur dioxide to sulfur. The hydrogen

35   sulfide- and sulfur dioxide-containing gas stream preferably is a tail gas stream from a Claus plant.

15

In general, Claus plants are operated to provide a small stoichiometric excess of hydrogen sulfide over sulfur dioxide, which normally would result in residual hydrogen sulfide after reaction of the sulfur dioxide and hydrogen sulfide. The composition of the gas stream may be adjusted, however, as described herein, to ensure essentially complete reaction of both hydrogen sulfide and sulfur dioxide to sulfur in the liquid sulfur. For example, it may be desirable to add oxygen to the tail gas stream to provide for conversion to hydrogen sulfide and hydrogen polysulfide in the liquid sulfur to sulfur. The Claus plant tail gas clean up procedure generally is carried out in the presence of a catalyst for the reaction of hydrogen sulfide with sulfur dioxide. Any of the Bronsted-Lowry bases mentioned herein may be employed. It may be desirable to provide a non-volatile catalyst in the sulfur.

The impeller generally is rotated about a substantially vertical axis at the submerged locati n within the liquid sulfur at a blade tip velocity (v_i) of at least about 150 in/sec (at least about 4 m/s), preferably at least about 350 in/sec (at least about 9 m/s), more preferably at least about 500 in/sec (preferably at least about 12.5 m/s), for example, up to and greater than about 700 in/sec (up to and greater than about 18 m/s), and draws liquid sulfur into the interi r of the shroud effecting vigorous circulation of liquid sulfur through the impeller and shroud combination.

The shear forces between the impeller blades and the plurality of openings in the shroud distribute the stripping gas in the liquid sulfur as bubbles to the interior of the shroud and forms a gas-liquid mixture of bubbles of the stripping gas in liquid sulfur contained within the shroud and effects intimate contact f the stripping gas and liquid sulfur at the submerged location while effecting shearing of the gas-liquid mixture within

the shroud and initiating and sustaining rapid mass transfer.

The gas-liquid mixture flows from within the shroud through and in contact with the openings therein to external of the shroud at a gas velocity index (GVI) generally of at least about 4 per second per opening, preferably at least about 18 per second per opening, more preferably at least about 24 per second per opening, which causes further shearing of the gas liquid mixture and further intimate contact of gaseous phase and liquid sulfur. The gas velocity index (GVI) more preferably is at least about 30 per second per opening, and may range to very high values, such as up to about 500 per second per opening, and often is in excess of about 100 per second per opening.

The gas velocity index (GVI) is determined by the expression:

$$GVI = \frac{QP}{4nA^2}$$

where Q is the volumetric flow rate of gas into the impeller (m^3/S), n is the number of openings in the shroud, A is the area of the opening (m^2) and P is the length of the perimeter of the opening (m).

An important operating parameter of the process is the relationship of the shroud diameter relative to the impeller diameter for a given GVI and impeller tip speed and this parameter may be termed the Effective Shear Index (ESI). The ESI is determined by the expression:

$$ESI = \frac{GVI}{v_i} \times \frac{(D_s - D_i)}{2} \times 100$$

wherein GVI is the gas velocity index (/s), v_i is the impeller blade tip velocity (m/s), and D_s and D_i are inside diameter of the shroud and outside diameter of the

17

impeller respectively (m). The method of the invention generally is carried out at an ESI value from about 1 to about 6000, preferably from about 10 to about 250, optimally about 50.

5   Another important operating parameter of the process of the invention is the relationship of the impeller diameter and height for a given volumetric gas flow rate and impeller tip speed and this parameter may be termed the Shear Effectiveness Index (SEI). The SEI is

10   determined by the relationship:

$$SEI=\frac{Q}{\pi hD_i v_i}X100$$

wherein Q is the volumetric gas flow rate into the impeller (m^3/s), h is the height of the impeller blades (m), D_i is the outside diameter of the impeller (m) and

15   v_i is the impeller blade tip velocity (m/s). The present invention generally employs an SEI value in the range of about 1 to about 25 and preferably about 2 to about 5. These parameters apply to self-induced systems with ut internal baffles as described in U.S. Patent N .

20   3,993,563 (Degner) and/or to those with externally-sparged gas. The ESI and SEI values employed herein preferably are determined for impeller tip speed velocities of at least about 350 in/sec (at least about 9 m/s).

25   A further important operating parameter of the process is the interrelationship of the density of the liquid phase, namely the liquid sulfur, processed by the present invention and the volumetric flow rate of gas into the reactor and this parameter may be termed the

30   Density Index (DI). The DI is determined by the expression:

18

$$DI = \frac{Q}{Q_i}\left[\frac{\rho_L - \rho_g}{\rho_{H2O} - \rho_{air}}\right]$$

where Q is the volumetric flow rate of the stripping gas to the impeller (m^3/s), Q_i is the self-induction flow rate of air into water (m^3/s), ρ_L is the density of the liquid

5   sulfur (kg/m^3), ρ_g is the density of the gas (kg/m^3), ρ_{H2O} is the density of water (kg/m^3) and ρ_{air} is the density of air (kg/m^3). The method of the invention generally is carried out at a DI value from about 1 to about 8, preferably about 3.

10   For efficient operation, the procedure is preferably effected at a Gas Displacement Index (GDI) value of about -0.50 to about 0.95 as determined by the relationship:

$$GDI = \frac{2V_i \cdot \omega - Q}{2V_i \cdot \omega}$$

where V_i is the volume swept by the impeller (m^3), ω is

15   the rate of rotation of the impeller (rad/s) and Q is the volumetric flow rate of the gas to the impeller (m^3/s), and a Mixing Index (MI) value of at least about -5 as determined by the relationship:

$$MI = \frac{2V_i \cdot \omega - Q}{Vr}$$

20   where V_i is the volume swept by the impeller (m^3), ω is the rate of rotation of the impeller (rad/s), Q is the volumetric flow rate of gas to the impeller (m^3/s) and V_r is the volume of the reactor (m^3).

DESCRIPTION OF PREFERRED EMBODIMENT

25   Referring to the drawings, Figure 1 shows a novel liquid sulfur degassing device 10 operated in accordance with one preferred embodiment of the inv ntion. The device 10 includes an enclosed housing 12 illustrated to

be of cylindrical shape but any convenient geometric shape may be adopted. It is preferred that the geometric shape of the housing may be such as to avoid dead zones in the liquid phase contained within the housing.

5   A liquid sulfur feed inlet pipe 14 communicates with the interior of the housing 12 through the lower wall 16 and an overflow outlet 18 for liquid sulfur allows liquid sulfur to overflow from the interior of the housing 18 following processing therein.

10   A gas inlet 20 communicates with a standpipe 22 or draft tube extending downwardly inside the housing 12 to below the level of the body of liquid sulfur 24 contained within the vessel to enable a stripping gas for hydrogen sulfide. The stripping gas generally is air but a sulfur

15   dioxide-containing gas stream may be employed. Steam may be employed in place of or in addition to air. The tail gas stream from a Claus plant also may be employed as the gas feed, thereby also effecting Claus plant tail gas clean up. As mentioned earlier, Claus plant tail gas

20   clean up also may be effected in liquid sulfur from which the stripping of hydrogen sulfide and/or polysulfide is not required, such as liquid sulfur which has been degassed according to the invention.

          The gas stream generally is of a volume to permit

25   purging of hydrogen sulfide released by the liquid sulfur following decomposition of hydrogen polysulfide from the vessel 10. Suitable Bronsted-Lowry catalysts included those having pK_b values of less than about 10 and preferably less than about 6, and may comprise amines

30   sparingly soluble in the liquid sulfur. The catalyst may be introduced to the interior of the shroud by any convenient means, such as transportation in the stripping gas stream or by direct introduction to the vortex in the shroud. If desired, a catalyst which is soluble in the

35   liquid sulfur may be contained therein.

20

Generally, the flow rate of the stripping gas stream may range upwardly from a minimum of about 50 cu.ft/min. (about 25 dm^3/s), for example, in excess of about 3000 cu.ft/min. (about 1400 dm^3/s), although much higher or

5   lower flow rates may be employed. The pressure drop across the unit may be quite low and may vary from about -3 to about +40 in. H_2O (from about -75 to about +1000 mm H_2O), preferably from about 0 to less than about 10 in. H_2O (250 mm H_2O). For larger units, employing a fan or a

10   blower to assist the gas flow rate to the impeller, the pressure drop may be greater. The flow rate is further defined by the DI values discussed above.

A drive shaft 26 extends into the vessel 10 and has an impeller 28 mounted at its lower end just below the

15   lower extremity of the standpipe 22. A drive motor (not shown) is operatively connected to the drive shaft 26 to effect rotation of the shaft 26 and hence the impeller 28.

The impeller 28 comprises a plurality of radially-

20   extending blades 30. The number of such blades may vary and generally at least four blades 30 are employed, as illustrated, with the blades being equi-angularly spaced apart. The impeller 28 is illustrated with the blades 30 extending vertically. However, other orientations of the

25   blades 30 are possible.

Generally, the standpipe 22 has a diameter dimension related to that of the impeller 28 and the ratio of the diameter of the standpipe 22 to that of the impeller 28 generally may vary from about 1:1 to about 2:1. However,

30   the ratio may be lower, if the impeller is mounted below the standpipe. The impeller 28 generally has a height which corresponds to an approximately 1:1 ratio with its diameter, but the ratio generally may vary from about 0.3:1 to about 3:1. As the stripping gas is drawn down

35   through the standpipe 22 by the action of the rotating impeller 28 and the liquid sulfur is drawn into the

21

impeller 28 thereby, the action of stripping gas and
liquid sulfur flow and rotary motion produce a vortex of
liquid sulfur in the standpipe and the region of the
impeller 28.   Alternatively, the stripping gas may be
5   introduced below the impeller 28 and drawn into the
interior of the shroud 32 by the action of the impeller
28.

The ratio of the cross-sectional area of the
shrouded impeller 28 to the cross-sectional area of the
10   apparatus 10 may vary widely.

Another function of the impeller 28 is to distribute
the introduced stripping gas bubbles within the liquid
sulfur in the interior of the shroud 34. This result is
achieved by rotation of the impeller 28, resulting in
15   shear of liquid sulfur and stripping gas to form bubbles
of relatively wide size distribution dimensioned so that
the largest are no more than about ¾ inch (20 mm) in
diameter.

A critical parameter in determining an adequate
20   shearing to form the gas bubbles is the velocity of the
outer tip of the blades 32. A blade tip velocity (v_i) of
at least about 150 in/sec (at least about 4 m/s) is
required to achieve efficient (i.e., 99%+) and rapid (of
the order of minutes residence time) removal of hydrogen
25   sulfide from liquid sulfur and conversion of hydrogen
polysulfide, preferably at least about 350 in/sec (at
least about 9 m/s), more preferably at least about 500
(at least 12.5), and up to and greater than 700 in/sec
(about 18 m/s).

30   The impeller 28 is surrounded by a cylindrical
stationary shroud 34 having a uniform array of circular
openings 36 through the wall thereof. The shroud 34
generally has a diameter slightly greater than the
standpipe 22. Although, in the illustrated embodiment,
35   the shroud 34 is right cylindrical and stationary, it is
possible for the shroud 34 to possess other shapes. For

22

example, the shroud 34 may be tapered, with the impeller 28 optionally also being tapered. In addition, the shroud 34 may be rotated, if desired, usually in the opposite direction to the impeller 28. Further, the
5   shroud 34 is shown as a separate element from the standpipe 22. However, the shroud 34 may be provided as an extension of the standpipe 22, if desired.

Further, the openings 36 in the shroud are illustrated as being circular, since this structure is
10   convenient. However, it is possible for the openings to have different geometrical shapes, such as square, rectangular or hexagonal. Further, all the openings 36 need not be of the same shape or size.

The shroud 34 serves a multiple function in the
15   device. Thus, the shroud 34 prevents gases from by-passing the impeller 28, assists in the formation of the vortex in the liquid sulfur necessary for gas induction, assists in achieving shearing as well as providing additional shearing and confines the gas-liquid mixture
20   and hence maintains the turbulence and agitation produced by the impeller 28. The effect of the impeller-shroud combination may be enhanced by the employment of a series of elongate baffles, provided on the internal wall of the shroud 34, preferably vertically extending from the lower
25   end to the upper end of the openings in the shroud. The gas-liquid mixture flows through and in contact with the openings 36 in the shroud which results in further shearing of the gas bubbles and further intimate contact of the gaseous and liquid phases.

30   The combined action of the impeller and shroud results in a rapid mass transfer of hydrogen sulfide into the stripping gas and catalyst into the sulfur, resulting in very rapid removal of dissolved hydrogen sulfide and decomposition of hydrogen polysulfides to sulfur and
35   hydrogen sulfide. The reactions are very rapid, in contrast to the prior art liquid sulfur degassing

operations. The combined action of the impeller and
shroud effects circulation of liquid sulfur within the
housing 12 and adequate mixing of the liquid sulfur in
the body of liquid sulfur external to the shroud 32 to
5   ensure the release of the stripping gas.

The openings 36 are dimensioned to permit a gas flow
rate therethrough corresponding to a gas velocity index
of at least about 4 per second per opening in the shroud,
preferably at least about 18 per second per opening and
10 more preferably at least about 30 per second per opening.

The shroud 34 is spaced only a short distance from
the extremity of the impeller blades 30, in order to
provide   and   promote   the   above-noted   functions.
Generally, the ratio of the diameter of the shroud 34 to
15 that of the impeller 28 generally is about 3:1 to about
1.1:1, preferably approximately 1.5:1. The relationship
of the shroud and impeller diameters may be further
particularized by the ESI and SEI indices discussed
above.

20   The openings 36 in the shroud 34 generally are
circular, although an equivalent effect can be achieved
using openings of large aspect ratio, such as slits.
When such circular openings are employed, the openings 36
generally are uniformly distributed over the wall of the
25 shroud 34 and usually are of equal size. The equivalent
diameter of the openings 36 often is less than about one
inch (25 mm) and generally should be as small as possible
without plugging, preferably about ¾ to about ⅝ inch
(about 10 to about 15 mm) in diameter, in order to
30 provide for the required gas flow therethrough. When the
openings 36 are of non-circular geometrical shape and of
aspect ratio which is approximately unity, then the area
of each such opening 36 generally is less than the area
of a circular opening having an equivalent diameter of
35 about one inch (25 mm), preferably about ¾ to about ⅝
inch (about 10 to about 15 mm). The openings have sharp

24

corners to promote shearing of th gas bubbles passing
through the openings and contacting the edges.

The shroud 34 is illustrated as extending downwardly
for the height of the impeller 28. It is possible for
5   the shroud 34 to extend above the height of the impeller
28 or for less than its full height, if desired.

In addition, in the illustrated embodiment, the
impeller 28 is located a distance corresponding to
approximately half the diameter of the impeller 28 from
10   the bottom wall of the reactor 10. It is possible for
this dimension to vary from less than about 0.25:1 to
about 1:1 or greater of the proportion of the diameter
dimension of the impeller. This spacing of the impeller
28 from the lower wall allows liquid sulfur to be drawn
15   into the area between the impeller 28 and the shroud 34
from the body of liquid sulfur 24 in the reactor 10. If
desired, a draft tube may be provided extending into the
body of the liquid sulfur from the lower end of the
impeller 28, to guide liquid into the region of the
20   impeller.

Following passage of the gas-liquid mixture through
the openings in the shroud a relatively quiescent zone is
provided in the body of liquid sulfur 24 where gas
bubbles disengage from the sulfur and provide a gaseous
25   phase in the head space above the liquid level of molten
sulfur in the vessel 10. A further shroud may be
provided surrounding the shroud 34 to promote additional
mixing.

The liquid sulfur degassing apparatus 10 provides a
30   very compact unit which rapidly and efficiently removes
hydrogen sulfide and hydrogen polysulfides from liquid
sulfur, in contrast to the large size holding tanks
commonly employed in the art.

The novel sulfur degassing procedure employed herein
35   may be effected as a single operation, or more
preferably, a plurality of individual contactors

connected in series, with each contactor having a hold-up
volume commensurate with the production rate of liquid
sulfur, thereby providing continuous processing of the
liquid sulfur. The individual contactors may vary in
5   hold-up capacity and residence time, depending on the
degassing requirements of the sulfur producing plant. A
typical operation effected in accordance with the
invention produces a high quality product with a total
hydrogen sulfide content of a few ppmw or less, or such
10   higher value as can be accepted. A polishing contactor,
designed to remove catalyst from the liquid sulfur can
further contribute to improve product quality. The gas
phases may be circulated countercurrently through the
contactors.

15   Any sulfur dioxide which may be formed as a result
of oxidation with air in later stages of processing with
low residual hydrogen sulfide levels may be reacted with
hydrogen sulfide in earlier stages, converting some of
the hydrogen sulfide present to elemental sulfur.

20   The processing of the liquid sulfur in the apparatus
10 produces a low volume effluent gas which is relatively
high in hydrogen sulfide content, along with some
volatile impurities and traces of sulfur vapor, which is
vented from the head space 38 above the body of liquid
25   sulfur 24 in the vessel 10 through a gaseous outlet 40.
This effluent stream may be disposed of by incineration,
or may be used as feed stream to a Claus plant for the
oxidation of hydrogen sulfide, or to another hydrogen
sulfide control process, such as by utilizing the
30   procedure of USP 5,174,973, referred to previously.

<u>EXAMPLES</u>

<u>Example 1</u>:

An experimental apparatus was set up having the
structure illustrated in Figure 1. Two contactors
35   differing in size were tested. A bench scale unit having
a volume of 9 litres (16 kg) was used primarily to

26

measure the removal rates of H_2S and H_2S_x by measuring concentrations over time. A 970 litre pilot scale unit (1.75 tonnes) was used primarily to measure reaction rates using a steady-state flow of liquid sulfur. Sulfur produced by the Claus process from two different gas plants was used as feedstock for the two units.

The operating parameters for the apparatus employed in generating the data shown in Figure 3 to 8 and 10 ar set forth in the following Table:

Figures	3, 4	5, 6	7	8, 10
v_i(in/sec)	640	356	640	640
GVI (/s)	.28.9	9.7	53.1	43.4
ESI	23.7	3.1	43.6	35.6
SEI	1.6	0.9	2.9	2.3
DI	1.9	1.0	3.5	2.9

The apparatus used to generate the data in Figure 5, 6 had an impeller 2 in. in diameter and 2 in. in height and a shroud having an inside diameter of 4.25 in., with 100 x ¾ in. diameter openings therethrough. The apparatus used to generate the data in the other Figures had an impeller 12.75 in. in diameter and 13 in. in height and a shroud having an inside diameter of 23.25 in., with 1824 x ½ in. diameter openings therethrough.

Samples of liquid sulfur were withdrawn at various locations and times and the concentration of the H_2S and H_2S_x measured using a Fourier Transform Infra Red (FTIR) spectrophotometer within a few minutes after sampling. An accessory system developed by Alberta Sulphur Research had permitted non-intrusive determination of the total residual H_2S ($H_2S+H_2S_x$) concentrati ns in liquid sulfur down t 4 ppmw. The absorptions by H_2S at 2570 cm^{-1} and

H_2S_x at 2497 cm^{-1} were calibrated and displayed in units of ppmw.

The contactors were operated using air as the stripping gas with and without added catalyst OPTI-MEEN 2200 (Betz Chemicals, Ltd, a proprietary aqueous solution of morpholine (10 to 30%) and cyclohexylamine (40 to 70%). A typical FTIR spectrum showing H_2S and H_2S_x in liquid sulfur feed is shown in Figure 2. The curves shown in Figure 3 present the H_2S and H_2S_x concentration plotted logarithmically against time for a typical experiment conducted with the pilot reactor using air as the stripping gas in the absence of catalyst. The steeply falling line at the left edge of the graph depicts the decrease in concentration of dissolved hydrogen sulfide, while the gradually sloped curve depicts the decrease in the concentration of polysulfides. Based on the slopes of these lines, the half-lives for H_2S and H_2S_x were calculated to be 0.75 and 48 minutes respectively.

Figure 4 contains a semi-logarithmic plot of the gaseous hydrogen sulfide concentration in the effluent gas against time. The very fast initial decrease in H_2S concentration can be attributed to the rapid degassing of hydrogen sulfide while the slow decrease in H_2S concentration corresponds to decomposition of H_2S_x.

Figure 5 shows the effect of the addition of a small amount of catalyst in a batch test, namely 4.8 ppmw of OPTI-MEEN 2200. As can be seen, the addition of the catalyst had a remarkable effect on the rate at which hydrogen polysulfides were converted to H_2S. Sulfur containing high initial concentrations of H_2S and H_2S_x was degassed using air as the stripping gas in the bench scale apparatus. Measurement of the hydrogen polysulfide concentration commenced about 30 minutes into the run, once the concentration fell within the calibrated range (<195 ppmw) and at various times over the next 25 minutes

to establish a reference half-life using air as the stripping gas. Fifty-eight minutes into the run, 0.08 mL of catalyst, corresponding to a nominal concentration of 4.8 ppmw, was injected into the stripping gas intake line

5 using a syringe. As can be seen from Figure 5, the half-life for the decrease in H_2S_x concentration with catalyst present was reduced to less than one minute from about 45 ± 15 minutes generally observed with air alone, corresponding to about a 40-fold increase in

10 decomposition rate.

Figure 6 contains FTIR spectra showing the history of H_2S and H_2S_x peaks at around the time of catalyst addition in Figure 5. A small H_2S peak, absent before the introduction of catalyst, appeared simultaneously

15 with the onset of the rapid depletion of H_2S_x. Concomitant with the progressive decrease in the H_2S_x peak, the H_2S rose to a maximum a short time later and then declined in parallel with the H_2S_x peak.

Batch tests using catalyst in the larger pilot-scale

20 contactor yielded results comparable with those obtained with the bench-scale apparatus. Figure 7 shows the spectra of sulfur samples taken from the contactor prior to and 70 seconds after injecting an amount of catalyst, nominally equivalent to 1.2 ppmw, into the air intake of

25 the large contactor. In the test of Figure 7, polysulfides concentration decreased with a half-life of around 0.5 minutes, again indicative of the powerful influence a very small amount of catalyst has on the polysulfide decomposition rate in the process of the

30 invention. As with the bench-scale unit, H_2S remained observable while H_2S_x was decomposing at a rapid rate. Moreover, the agreement between declining concentration rates observed with the two contactors widely different in size cnfirmed the validity of the scale-up factors

35 used in the design of the larger unit.

A visual comparison of the two spectra in Figure 7 reveals that many of the peaks, like the H_2S peak, rapidly decrease in height over a short time. The majority of the peaks declined exponentially with half-

5   lives between 0.3 and 0.8 minutes, quite within the range seen for H_2S. This is the case for water, which absorbs in the region over 4000 cm^{-1} to 3400 cm^{-1} and at 1591 cm^{-1}. It may be reasonably generalized that any volatile substance, such as water CO_2, SO_2, COS, CS_2 and

10   hydrocarbons also may be effectively purged, along with the catalyst itself.

Example 2:

Although batch studies of the time dependency of the H_2S and H_2S_x concentrations provided a clear picture of

15   the capabilities of the process as outlined in Example 1, the performance of the pilot-scale contactor using a steady-state flow of feed sulfur gave a much better idea of the process in its practical application. Sulfur flowrates were varied between 34 and 53 tonnes/h.

20   Catalyst was introduced directly into the liquid sulfur in quantities ranging from 4.8 to 10.8 ppmw. N significant effect on the rates of decrease in concentration of H_2S and H_2S_x was observed on varying the sulfur temperature from 140° to 152°C.

25   The spectrum of contactor feed and contents for a typical flowthrough test are presenting in Figure 8. The marked decrease in the absorption by H_2S, H_2S_x and other volatiles qualitatively suggests that efficient degassing of the various substances is taking place.

30   Measurement of the respective concentrations indicate that 61% of the H_2S and 79% of the H_2S_x was removed during the hold-up time of 2.5 minutes, corresponding to half-lives of 0.76 and 0.46 minutes, respectively. It is noted in Figure 8 that other

35   volatile substances in the feed are as readily degassed

30

in flowthrough tests as in batch tests (see Figure 7), with rates comparable to the degassing of H_2S.

Figure 9 summarizes the results of the continuous flow experiments, showing the half-life of the H_2S_x
5   decomposition reaction as a function of catalyst concentration, expressed in ppmw with respect to the sulfur. The vertical lines represent the range of values for several sets of measurements taken at a particular catalyst concentration. In many instances where the
10 catalyst concentration was above 8 ppmw, the H_2S_x concentrations in the contactor were reduced to levels below the measurement sensitivity (< 2 ppmw) of the FTIR system. Since the final concentration was not known in these cases, quantitative rate data were not acquired,
15 although it is noted that the half-life was below 0.5 minutes. This Figure suggests that the half life of polysulfide concentration decrease varies approximately linearly with catalyst concentration in the region between 4 and 8 ppmw. The curve, however, rises very
20 steeply as the catalyst concentration approaches zero, since the half-life measured in batch tests with no catalyst present was approximately 45 ± 15 minutes.

Degassification of sulfur down to very low levels of H_2S and H_2S_x was routinely achieved with the pilot scale
25 contactor. Figure 10 compares the spectrum of a sulfur sample taken at the start of one of the tests to one taken after approximately three passes through the pilot-scale contactor. Very low residual H_2S and H_2S_x concentrations were achieved, (since the H_2S peak is
30 hardly detectable, and the H_2S_x concentration is well below the measurement accuracy) using a flowthrough contactor of a size that would comfortably handle the production of many existing sulfur plants.
Example 3:

35 During the experiments reported in Examples 1 and 2, it became apparent that the strength properties of

(solidified) sulfur samples taken from the contactor varied significantly. Those samples that contained a modest amount of residual catalyst were brittle and crumbly whereas those samples that contained less of the catalyst were very hard to break.

This effect was substantiated in an experiment where the H_2S and H_2S_x concentrations in 75 tonnes of sulfur were reduced below 2 ppmw by degassing using a catalyst concentration of approximately 10 ppmw. After the H_2S and H_2S_x were essentially eliminated, half of the liquid sulfur was solidified using a granulation process, and samples of the product set aside for friability testing according to SUDIC procedures (ref. 2). With liquid sulfur feed containing residual amounts of catalyst but very little H_2S and H_2S_x, the friability averaged 3.1%. The remaining sulfur was then circulated once more through the contactor to degas as much of the volatile catalyst as possible by contacting the sulfur with air only.

After this simple treatment, the sulfur was solidified as before. The friability of the granulated product, in this case produced from liquid sulfur with a reduced amount of catalyst, averaged 0.7%.

Based on these comparative results, it appears that the presence of the catalyst and possibly other impurities, even in concentrations of a few ppmw, can have a significant effect on product quality. However, the degassing process provided herein has the capability to overcome any detrimental effects linked to catalyst contamination by dedicating a polishing contactor to the task of degassing the residual catalyst from the sulfur.
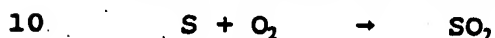
Example 4:

During the course of sulfur degassification tests with the pilot-scale unit described in Example 1 using air as the stripping gas and continuous sulfur flows, a determination was made of SO_2 content of the off-gas

stream as a function of catalyst concentration. During
these experiments, the following operating parameters
were employed:

V_i = 350 in/s, GVI = 34.8/s, ESI = 11.2, SEI = 3.3

5   and DI = 5. The data obtained was plotted graphically
and appears as Figure 11.

As is seen therein, in the absence of catalyst
(OPTI-MEEN 2200) 25 to 42 ppmw or approximately 0.01
mol/min of sulfur dioxide is produced by the reaction:

10        $S + O_2 \rightarrow SO_2$

This production rate decreased to 0 mol/min when the
catalyst concentration was in the range of 4.4 to 5.0
ppmw. A likely explanation for this observation is an
increased rate of a catalysed Claus reaction in the

15   liquid sulfur:

H_2S and/or $H_2S_x + SO_2 \rightarrow S + H_2O$

In another series of experiments, on this occasion
using the bench-scale unit described in Example 1, with
nitrogen containing a small amount of sulfur dioxide as

20   the stripping gas and a batch sulfur with no catalyst,
the effluent concentrations of sulfur dioxide and
hydrogen sulfide were determined. The parameters of
operation are those for the bench-scale unit enumerated
in Example 1 for Figures 5 and 6. The effluent

25   concentrations were as set forth in the following Table:

Time (min)	$[SO_2]$ ppmv	$[H_2S]$ ppmv
0	120	0
4	>120	0
13	1000	0
26	200	0

The data presented in this Table provides additional evidence of the existence of a Claus reaction in the liquid sulfur.

SUMMARY OF DISCLOSURE

5   In summary of this disclosure, the present invention provides a novel method of degassing liquid sulfur to remove hydrogen sulfide and hydrogen polysulfides therefrom by a stripping gas in the presence of a catalyst. The hydrogen sulfide is rapidly and
10 efficiently stripped and the hydrogen polysulfides are decomposed to sulfur and hydrogen sulfide, using an impeller-shroud combination, generally in conjuncti n with specific operating parameters. The present invention further provides a novel method of effecting
15 the Claus reaction, particularly for Claus plant tail gas clean up, by employing the impeller-shroud combination and liquid sulfur as the medium in which sulfur dioxide and hydrogen sulfide react to form sulfur. Claus plant tail gas also may be used as the stripping gas for liquid
20 sulfur containing hydrogen sulfide and hydrogen polysulfides. Modifications are possible within the scope of this invention.

34

REFERENCES

1. NIOSH, "Criteria for a Recommended Standard, Occupational Exposure to Hydrogen Sulfide", National Institute for Occupational Safety and Health, Cincinnati OH, 1977.

2. Sampling and Testing of Sulphur Forms, Sulphur Development Institute of Canada, 1978.

35

CLAIMS

What we claim is:

1.   A method of removing hydrogen sulfide and hydrogen polysulfides from liquid sulfur, which comprises:

providing a rotary impeller comprising a plurality of blades at a submerged location in said liquid sulfur surrounded by a shroud through which are formed a plurality of openings,

feeding a stripping gas for hydrogen sulfide to said submerged location while providing a Bronsted-Lowry base catalyst for the conversion of hydrogen polysulfides to hydrogen sulfide thereat,

rotating said impeller about a substantially vertical axis at a speed sufficient to draw liquid sulfur into the interior of the shroud and to distribute said stripping gas as bubbles in said liquid sulfur to the interior of said shroud and to form a gas-liquid mixture of bubbles of said gas in said liquid sulfur contained within said shroud,

flowing said gas-liquid mixture from within the interior of shroud through and in contact with said openings to external of said shroud, and

removing said stripping gas from the liquid sulfur.

2.   The method of claim 1 wherein said stripping gas is steam and said steam also provides said Bronsted-Lowry base catalyst.

3.   The method of claim 1 wherein said stripping gas is an oxidizing gas.

4.   The method of claim 3 wherein said oxidizing gas is air.

5.   The method of claim 1 wherein said stripping gas is a tail gas stream from a Claus plant.

6.   The method of claim 5 wherein said Claus plant tail gas stream contains a stoichiometric excess of sulfur dioxide with respect to hydrogen sulfide to effect

36

substantially complete conversion of hydrogen sulfide to sulfur in said liquid sulfur.

7.   The method of claim 5 wherein said Claus plant tail gas stream contains sufficient oxygen to provid a stoichiometric excess of sulfur dioxide with respect to hydrogen sulfide in said liquid sulfur.

8.   The method of claim 5 wherein a catalyst for conversion of hydrogen sulfide to sulfur by reaction with sulfur dioxide.

9.   The method of claim 3 wherein said oxidizing gas is sulfur dioxide in sufficient quantity to convert substantially all hydrogen sulfide present in the liquid sulfur and produced by decomposition of hydrogen polysulfides to sulfur.

10.   The method of claim 1 wherein said Bronsted-Lowry base catalyst has a pK_b value of less than about 10.

11.   The method of claim 10 wherein said pK_b value is less than about 6.

12.   The method of claim 11 wherein said Bronsted-Lowry base catalyst comprises ammonia or an amine.

13.   The method of claim 12 wherein said amine is cyclohexylamine or morpholine.

14.   The method of claim 12 wherein said catalyst is used in an amount of about 10 ppbw to about 10 ppmw relative to the weight of sulfur.

15.   The method of claim 12 wherein said catalyst is employed in an amount from about 1 to about 5 ppmw relative to the weight of sulfur.

16.   The method of claim 12 wherein said Bronsted-Lowry base catalyst is provided at said submerged location by transportation thereto.

17.   The method of claim 16 wherein said transportation is effected by introducing said catalyst into the liquid sulfur flowing int a vessel containing the same and/or by introducing the catalyst int the vessel, so as to be

transported to said submerged location by circulati n of liquid sulfur in the vessel.

18. The method of claim 16 wherein said transportation is effected by said stripping gas.

19. The method of claim 16 wherein said transportation is effected by introducing said catalyst directly into a vortex formed by said rotation of said impeller within the shroud.

20. The method of claim 19 wherein said stripping gas has a temperature at least about 20°C cooler than said liquid sulfur.

21. The method of claim 20 wherein said stripping gas has a temperature of less than about 100°C.

22. The method of claim 12 wherein said Bronsted-Lowry base catalyst is a volatile amine soluble in said liquid sulfur to facilitate removal from said liquid sulfur.

23. A method of removing hydrogen sulfide and hydrogen polysulfides from liquid sulfur, which comprises:

providing a rotary impeller comprising a plurality of blades at a submerged location in said liquid sulfur surrounded by a shroud through which are formed a plurality of openings,

feeding a stripping gas for hydrogen sulfide to said submerged location,

rotating said impeller about a substantially vertical axis at a speed corresponding to a blade tip velocity (vi) of at least about 150 in/sec (at least about 4 m/s) so as to draw liquid sulfur into the interior of the shroud and to generate sufficient shear forces between said impeller and said plurality of openings in said shroud to distribute said stripping gas as bubbles in said liquid sulfur to the interior of said shroud and to effect intimate contact of said gas and said liquid sulfur at said submerged l cation so as to form a gas-liquid mixture of bubbles of said gas in said liquid sulfur contained within said shroud while

effecting shearing of said gas-liquid mixture within said shroud, and

flowing said gas-liquid mixture from within the interior of shroud through and in contact with said openings to external of said shroud at a gas velocity index (GVI) of at least about 4 per second per opening in said shroud so as to effect further shearing of the gas-liquid mixture and further intimate contact of said gas and said liquid sulfur,

said gas velocity index (GVI) being determined by the expression:

$$GVI = \frac{QP}{4nA^2}$$

where Q is the volumetric flow rate of gas into the impeller (m^3/s), n is the number of openings in the shroud, A is the area of the opening (m^2) and P is the length of the perimeter of the opening (m),

said method being carried out:

(a) at an Effective Shear Index (ESI) value of about 1 to about 6000 as determined by the relationship:

$$ESI = \frac{GVI}{V_i} X \frac{(D_s - D_i)}{2} X 100$$

where D_s is inside diameter (m) of the shroud and D_i is the outside diameter (m) of the impeller,

(b) at a Shear Effective Index (SEI) value of about 1 to about 25 as determined by the relationship:

$$SEI = \frac{Q}{\pi h D_i v_i} X 100$$

where h is the height of the impeller (m), and

(c) at a Density Index (DI) value of about 1 to about 8 as determined by the relationship:

$$DI = \frac{Q}{Q_i}\left[\frac{\rho_L - \rho_g}{\rho_{H2O} - \rho_{air}}\right]$$

where Q_i is the self-induction flow rate of air into water (m^3/s), ρ_L is the density of the liquid sulfur (kg/m^3), ρ_g is the density of the gas (kg/m^3), ρ_{H2O} is the density of water (kg/m^3) and ρ_{air} is the density of air (kg/m^3).

24. The method of claim 23 wherein said blade tip velocity is at least about 350 in/sec (at least about 12.5 m/s).

25. The method of claim 23 wherein said blade tip velocity is at least about 500 in/sec. (at least about 12.5 m/s).

26. The method of claim 23 wherein said gas velocity index is at least about 18 per second per opening.

27. The method of claim 23 wherein said gas velocity index is at least about 24 per second per opening.

28. The method of claim 23 wherein said gas velocity index is from about 30 to about 500 per second per opening.

29. The method of claim 23 wherein said blade tip velocity is at least about 500 in/sec. (about 12.5 m/s) and said gas velocity index is at least about 30 per second per opening.

30. The method of claim 23 wherein said ESI value is determined at a v_i value of at least about 350 in/sec. (at least about 9 m/s).

31. The method of claim 23 wherein said SEI value is determined at v_i value of at least about 350 in/sec. (at least 9 m/s).

32. The method of claim 23 wherein said ESI value is about 10 to about 250 and is carried out at a Shear Effectiveness Index (SEI) value of about 4 to about 5.

33. The method of claim 32 wherein said SEI value is about 3.

34.   The method of claim 23 which is carried out in the presence of a Bronsted-Lowry base catalyst for the conversion of hydrogen polysulfide to hydrogen sulfide.

35.   The method of claim 23 wherein said stripping gas is steam, an oxidizing gas, or a tail gas stream from a Claus plant.

36.   The method of claim 34 wherein said catalyst is ammonia or an amine.

37.   The method of claim 36 wherein said amine is cyclohexylamine, morpholine or a mixture thereof.

38.   The method of claim 36 wherein said catalyst is used in an amount of about 10 ppbw to about 10 ppmw based on the weight of sulfur.

39.   The method of claim 36 wherein said catalyst is employed in an amount from about 1 to about 5 ppmw based on the weight of sulfur.

40.   The method of claim 34 wherein said Bronsted-Lowry base catalyst is provided at said submerged location by transportation thereto.

41.   The method of claim 34 wherein said transportation is effected by introducing said catalyst into the liquid sulfur flowing into a vessel containing the same and/or by introducing the catalyst into the vessel, so as to be transported to said submerged location by circulation of liquid sulfur in the vessel.

42.   The method of claim 40 wherein said transportation is effected by said stripping gas.

43.   The method of claim 40 wherein said transportation is effected by introducing said catalyst directly into a vortex formed by said rotation of said impeller within the shroud.

44.   The method of claim 43 wherein said stripping gas has a temperature at least about 20°C cooler than said liquid sulfur.

45.   The method of claim 44 wherein said stripping gas has a temperature of less than about 100°C.

46. The method of claim 34 wherein said Bronsted-Lowry base catalyst is a volatile amine soluble in said liquid sulfur to facilitate removal from said liquid sulfur.

47. The method of claim 1 or 23 which is effected at a sulfur temperature of about 120° to about 160°C.

48. The method of claim 47 wherein said sulfur temperature is about 125° to about 155°C.

49. The method of claim 1 or 23 wherein said liquid sulfur is treated in a series of procedures as defined in claim 1 effected in series-connected vessels.

50. The method of claim 49 wherein any sulfur dioxide formed in a later one of said series-connected vessels is recycled to an earlier one of said series-connected vessels for conversion to sulfur by reaction with hydrogen sulfide therein.

51. The method of claim 49 wherein residual soluble catalyst is stripped from the liquid sulfur following said series of procedures.

52. The method of claim 23 which is carried out at a Gas Displacement Index (GDI) value of about -0.5 to about 0.95 as determined by the relationship:

$$GDI = \frac{2V_i . \omega - Q}{2V_i . \omega}$$

where V_i is the volume swept by the impeller (m³), ω is the ratio of rotation of the impeller (rad/s) and Q is the volumetric flow rate of gas in the impeller (m³/s).

53. The method of claim 23 or 52 which is carried out at a Mixing Index (MI) value of at least about -5 as determined by the relationship:

$$MI = \frac{2V_i . \omega - Q}{V_r}$$

where V_i is the volume swept by the impeller (m³), ω is the rate of rotation of the impeller (rad/s), Q is the

42

volumetric flow rate of gas to the impeller (m^3/s) and V_r is the volume of the reactor (m^3).

54. A method for the processing of a hydrogen sulfid - and sulfur dioxide-containing gas stream to remove at least one of the components therefrom, which comprises:

providing a rotary impeller comprising a plurality of blades at a submerged location in said liquid sulfur surrounded by a shroud through which are formed a plurality of openings,

feeding said gas stream to said submerged locati n,

rotating said impeller about a substantially vertical axis at a speed sufficient to draw liquid sulfur into the interior of the shroud and to distribute said gas stream as bubbles in said liquid sulfur to the interior of said shroud and to form a gas-liquid mixture of bubbles of said gas stream in said liquid sulfur contained, within said shroud, and

flowing said gas-liquid mixture from within the interior of shroud through and in contact with said openings to external of said shroud, thereby to effect reaction between hydrogen sulfide and sulfur dioxide to sulfur.

55. The method of claim 54 wherein said hydrogen sulfide and sulfur dioxide-containing gas stream is a tail gas stream from a Claus plant.

56. The method of claim 55 wherein said Claus plant tail gas stream contains a stoichiometric excess of sulfur dioxide with respect to hydrogen sulfide to effect substantially complete conversion of hydrogen sulfide to sulfur in said liquid sulfur.

57. The method of claim 55 wherein said Claus plant tail gas stream contains sufficient oxygen to provide a stoichiometric quantity or excess of sulfur dioxide with respect to hydrogen sulfide in said liquid sulfur, whereby substantially all of the hydrogen sulfide and

43

sulfur dioxide in said tail gas stream is removed in the liquid sulfur.

58. The method of claim 55 wherein a catalyst f r conversion of hydrogen sulfide to sulfur by reaction with sulfur dioxide is provided in said liquid sulfur at said submerged location.

59. The method of claim 58 wherein said catalyst is a Bronsted-Lowry base catalyst having a pK_b of less than about 10.

60. The method of claim 59 wherein said pK_b value is less than about 6.

61. The method of claim 60 wherein said Bronsted-Lowry base catalyst is provided at said submerged location by transportation thereto.

62. The method of claim 60 wherein said transportation is effected by introducing said catalyst into the liquid sulfur flowing into a vessel containing the same and/or by introducing the catalyst into the vessel, so as to be transported to said submerged location by circulation of liquid sulfur in the vessel.

63. The method of claim 61 wherein said transportation is effected by said tail gas stream.

64. The method of claim 61 wherein said Bronsted-Lowry base catalyst is a volatile amine soluble in said liquid sulfur to facilitate removal from said liquid sulfur.

65. The method of claim 58 wherein said catalyst is substantially non-volatile and is dissolved in said liquid sulfur.

66. A method for the processing of a hydrogen sulfide- and sulfur dioxide-containing gas stream, which comprises:

providing a rotary impeller comprising a plurality of blades at a submerged location in said liquid sulfur surrounded by a shroud through which are formed a plurality of openings,

feeding said gas stream to said submerged location,

44

rotating said impeller about a substantially vertical axis at a speed corresponding to a blade tip velocity (v_i) of at least about 150 in/sec (at least about 4 m/s) so as to draw liquid sulfur into the interior of the shroud and to generate sufficient shear forces between said impeller and said plurality of openings in said shroud to distribute said gas stream as bubbles in said liquid sulfur to the interior of said shroud and to effect intimate contact of said gas stream and said liquid sulfur at said submerged location so as to form a gas-liquid mixture of bubbles of said gas in said liquid sulfur contained within said shroud while effecting shearing of said gas-liquid mixture within said shroud, and

flowing said gas-liquid mixture from within the interior of shroud through and in contact with said openings to external of said shroud at a gas velocity index (GVI) of at least about 4 per second per opening in said shroud so as to effect further shearing of the gas-liquid mixture and further intimate contact of said gas stream and said liquid sulfur, whereby reaction is effected between hydrogen sulfide and sulfur dioxide contained in said gas stream in the presence of liquid sulfur to form sulfur,

said gas velocity index (GVI) being determined by the expression:

$$GVI = \frac{QP}{4nA^2}$$

where Q is the volumetric flow rate of gas into the impeller (m^3/s), n is the number of openings in the shroud, A is the area of the opening (m^2) and P is the length of the perimeter of the opening (m),

said method being carried out:

(a) at an Effective Shear Index (ESI) value of about 1 to about 6000 as determined by the relationship:

$$ESI = \frac{GVI}{V_l} X \frac{(D_s - D_i)}{2} X 100$$

where D_s is inside diameter (m) of the shroud and D_i is the outside diameter (m) of the impeller,

    (b)   at a Shear Effective Index (SEI) value of ab ut 1 to about 25 as determined by the relationship:

$$SEI = \frac{Q}{\pi h D_i V_l} X 100$$

where h is the height of the impeller (m), and

    (c)   at a Density Index (DI) value of about 1 to about 8 as determined by the relationship:

$$DI = \frac{Q}{Q_i} \left[\frac{\rho_L - \rho_g}{\rho_{H2O} - \rho_{air}} \right]$$

where Q_i is the self-induction flow rate of air into water (m^3/s), ρ_L is the density of the liquid sulfur (kg/m^3), ρ_g is the density of the gas (kg/m^3), ρ_{H2O} is the density of water (kg/m^3) and ρ_{air} is the density of air (kg/m^3).

67.   The method of claim 66 wherein said blade tip velocity is at least about 350 in/sec (at least about 9 m/s).

68.   The method of claim 66 wherein said gas velocity index is at least about 18 per second per opening.

69.   The method of claim 66 wherein said hydrogen sulfide and sulfur dioxide-containing gas stream is a tail gas stream from a Claus plant.

70.   The method of claim 69 wherein said Claus plant tail gas stream contains a stoichiometric excess of sulfur dioxide with respect to hydrogen sulfide to effect substantially complete conversion f hydrogen sulfide to sulfur in said liquid sulfur.

71.   The method of claim 69 wherein said Claus plant tail gas stream contains sufficient oxygen to provide a stoichiometric quantity or excess of sulfur dioxide with respect to hydrogen sulfide in said liquid sulfur, whereby substantially all of the hydrogen sulfide and sulfur dioxide in said tail gas stream is removed in the liquid sulfur.

72.   The method of claim 66 wherein a catalyst for conversion of hydrogen sulfide to sulfur by reaction with sulfur dioxide is provided in said liquid sulfur at said submerged location.

73.   The method of claim 72 wherein said catalyst is a Bronsted-Lowry base catalyst having a pK_b of less than about 10.

74.   The method of claim 73 wherein said pK_b value is less than about 6.

75.   The method of claim 74 wherein said Bronsted-Lowry base catalyst is provided at said submerged location by transportation thereto.

76.   The method claim 72 wherein said catalyst is provided in said liquid sulfur at said submerged location by introducing the catalyst directly into a vortex formed by rotation of the impeller within the shroud.

77.   The method of claim 66 wherein said catalyst is substantially non-volatile and is dissipated in said liquid sulfur.

78.   The method of claim 66 which is carried out at a Gas Displacement Index (GDI) value of about -0.5 to about 0.95 as determined by the relationship:

$$GDI = \frac{2V_i \cdot \omega - Q}{2V_i \cdot \omega}$$

where V_i is the volume swept by the impeller (m^3), ω is the ratio of rotation of the impeller (rad/s) and Q is the volumetric flow rate of gas in the impeller (m^3/s).

47

79.   The method f claim 66 or 78 which is carried out at
a Mixing Index (MI) value of at least about 0.1 as
determined by the relationship:

$$MI = \frac{2V_i . \omega - Q}{V_r}$$

where V_i is the volume swept by the impeller (m^3), ω is
the rate of rotation of the impeller (rad/s), Q is the
volumetric flow rate of gas to the impeller (m^3/s) and $\dot{V}_r$
is the volume of the reactor (m^3).

80.   The method of claim 66 which is effected at sulfur
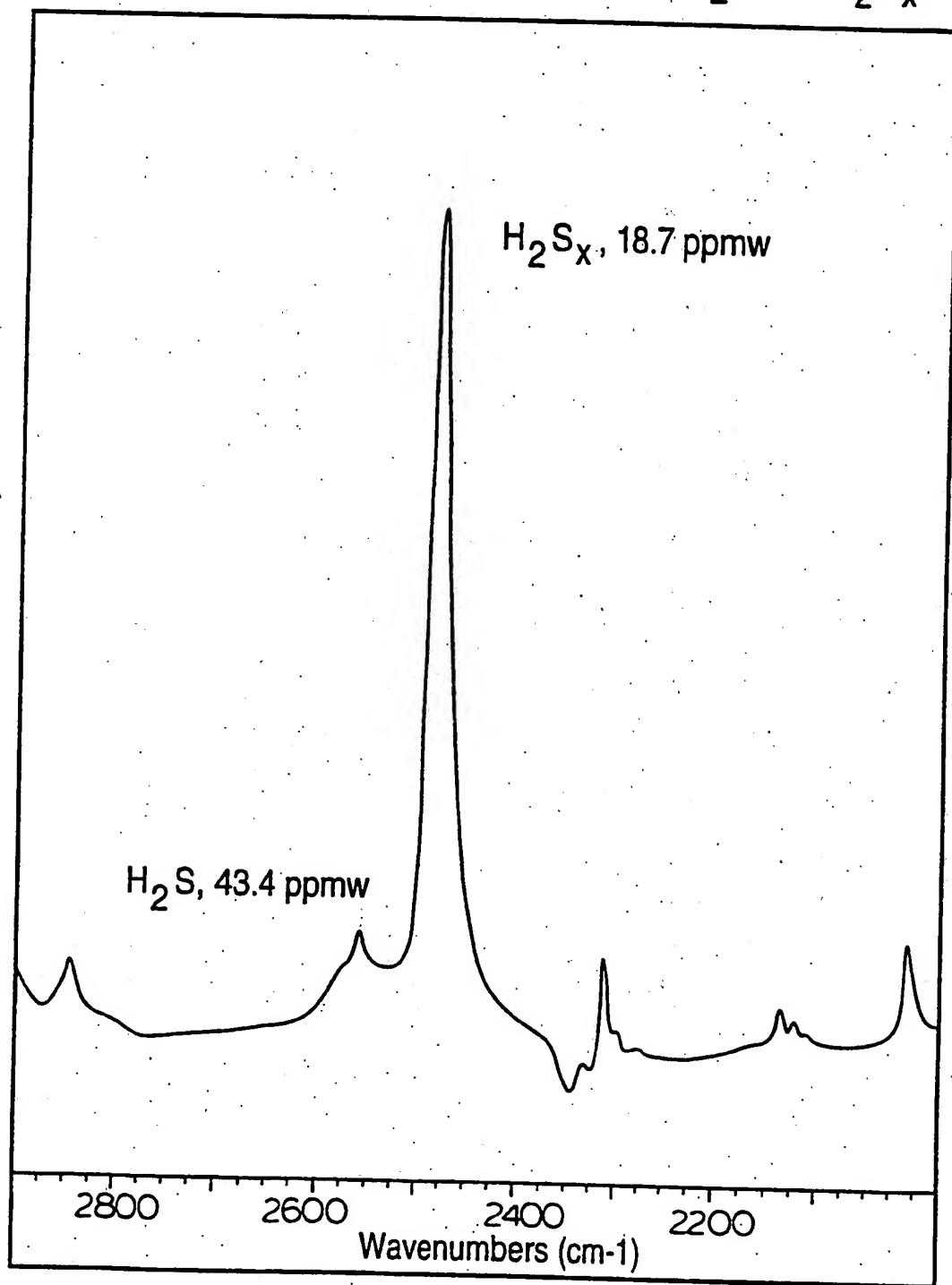temperature of about 120° to about 160°C.

FIG.1

FTIR Spectrum of Liquid Sulphur With Residual H_2S and H_2S_x

FIG.2.

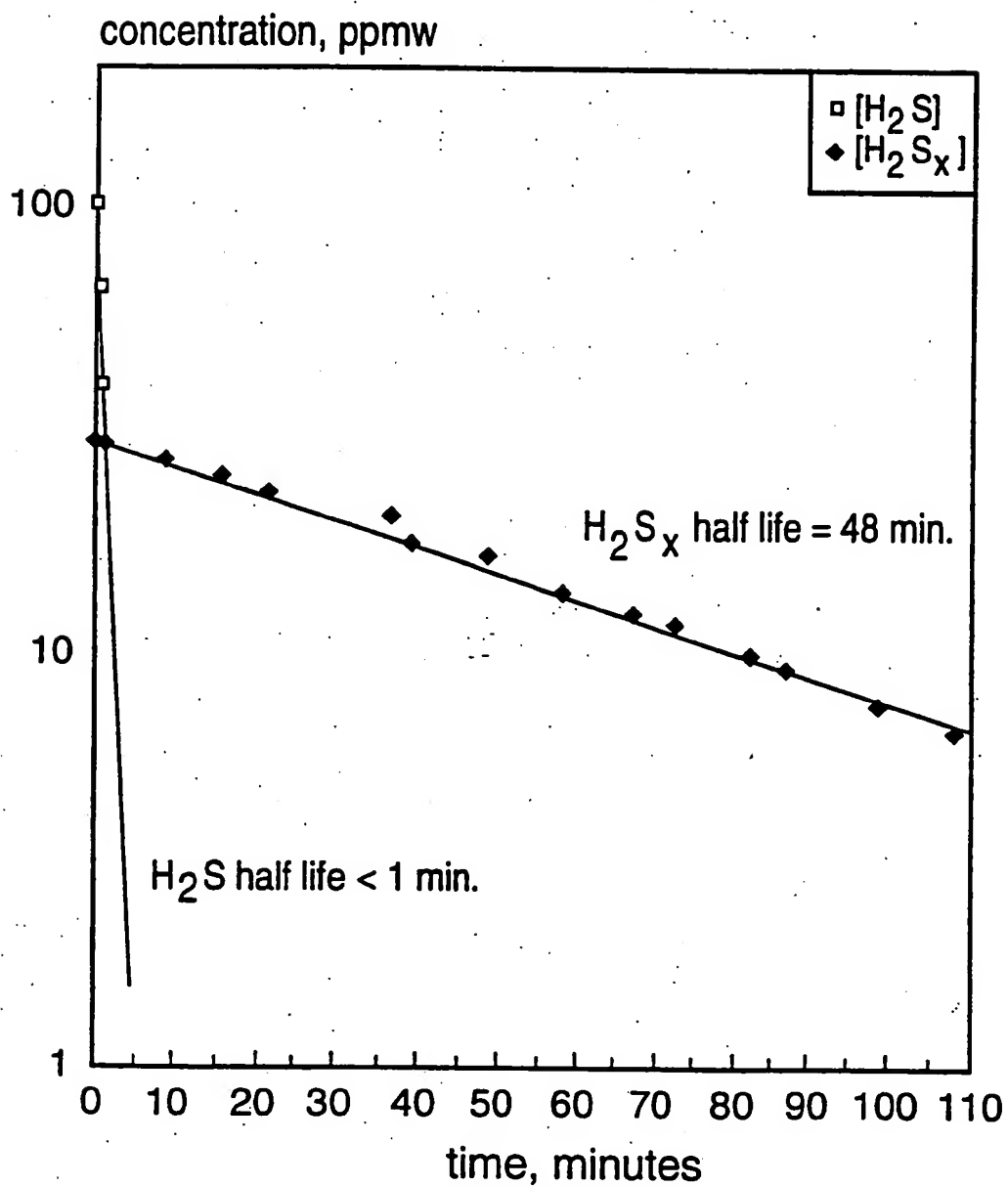Concentration Decrease of $H_2 S$ and $H_2 S_x$
Pilot-scale Contactor Using Air Sweep

FIG.3.

4 /11

Effluent [H$_2$S] vs. Time
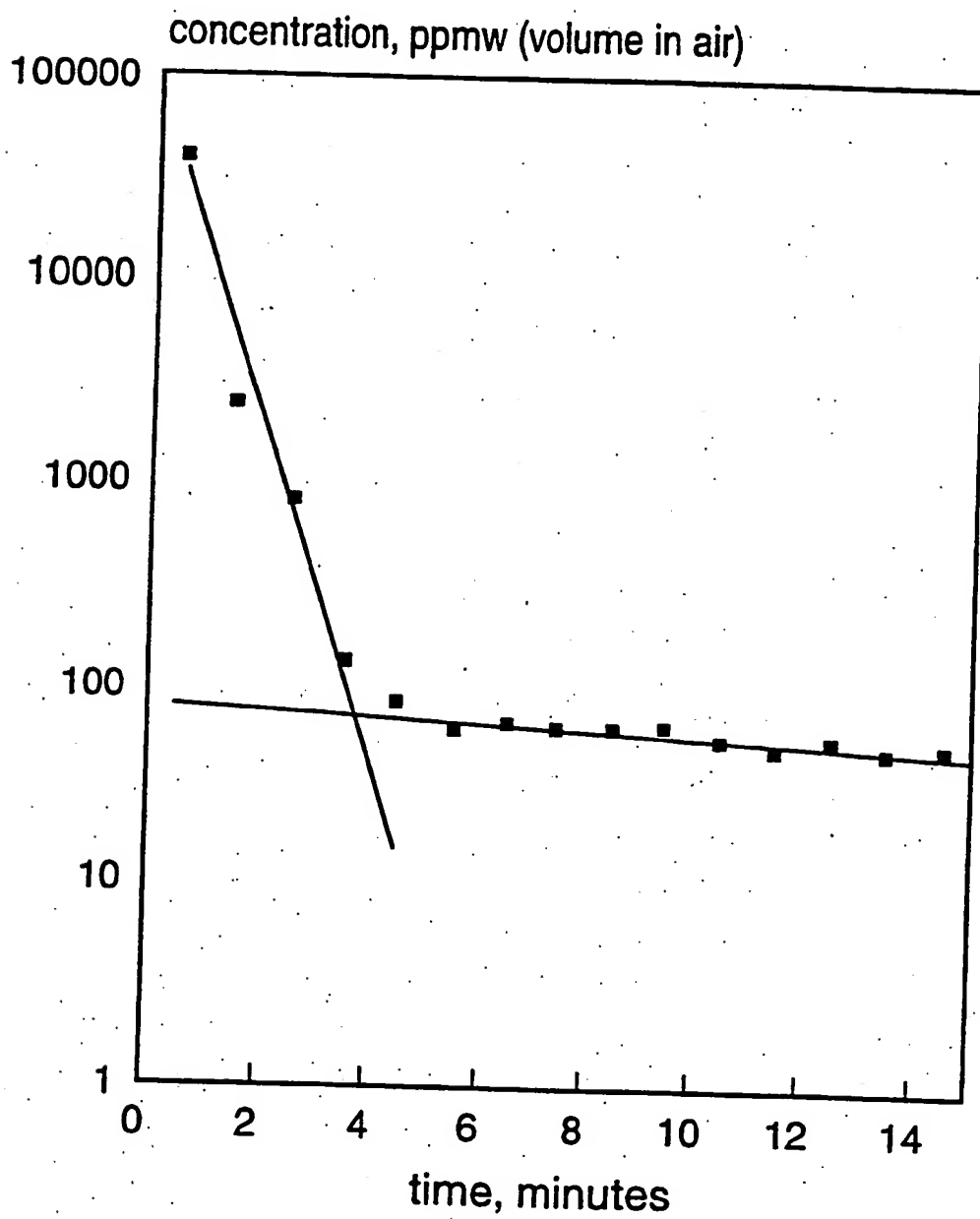Pilot-scale Contactor Using Air Stripping Gas

FIG.4.

Effect of Catalyst on the $H_2 S_x$ Concentration Reduction Rate.
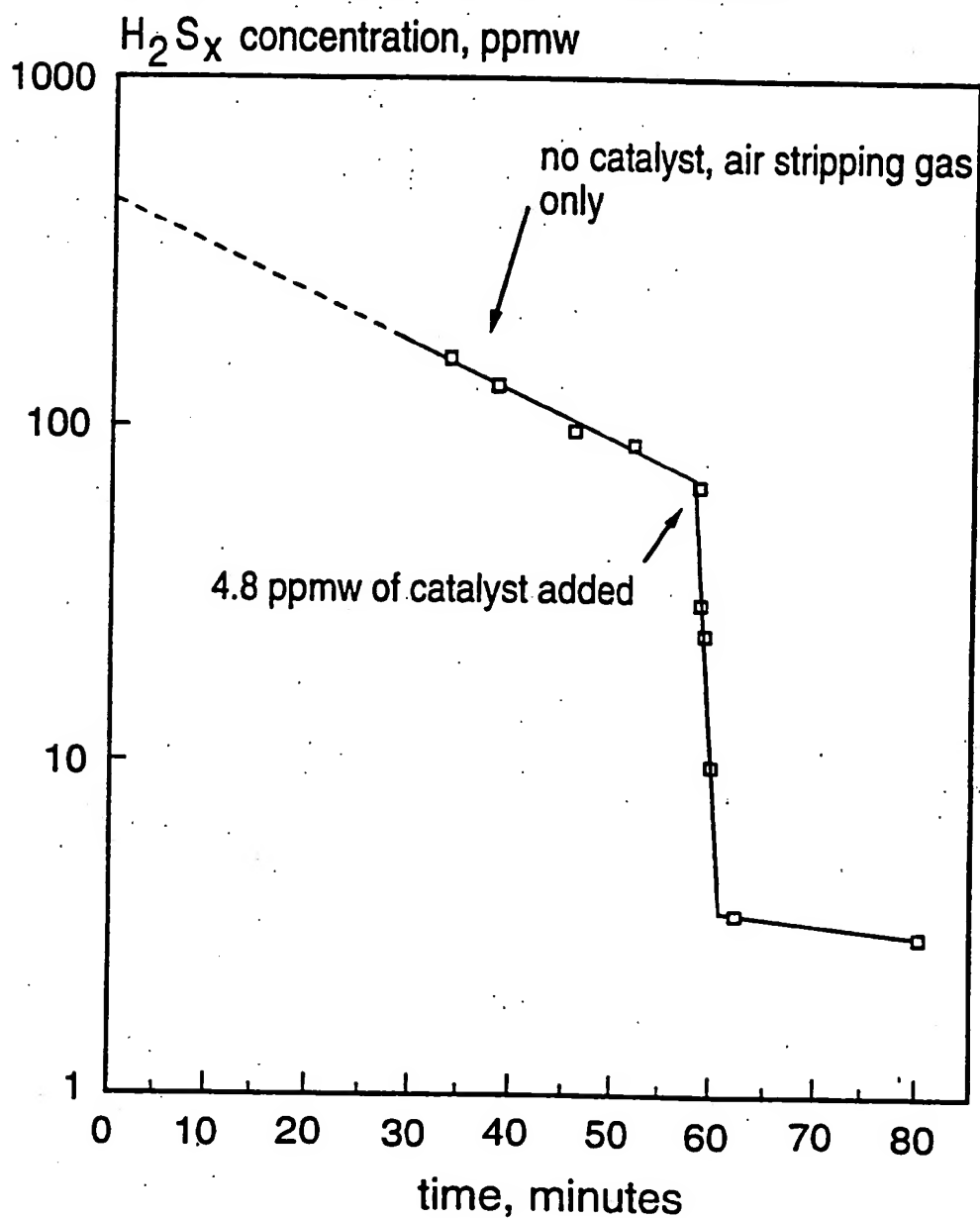Bench-scale contactor using air stripping gas

FIG.5.

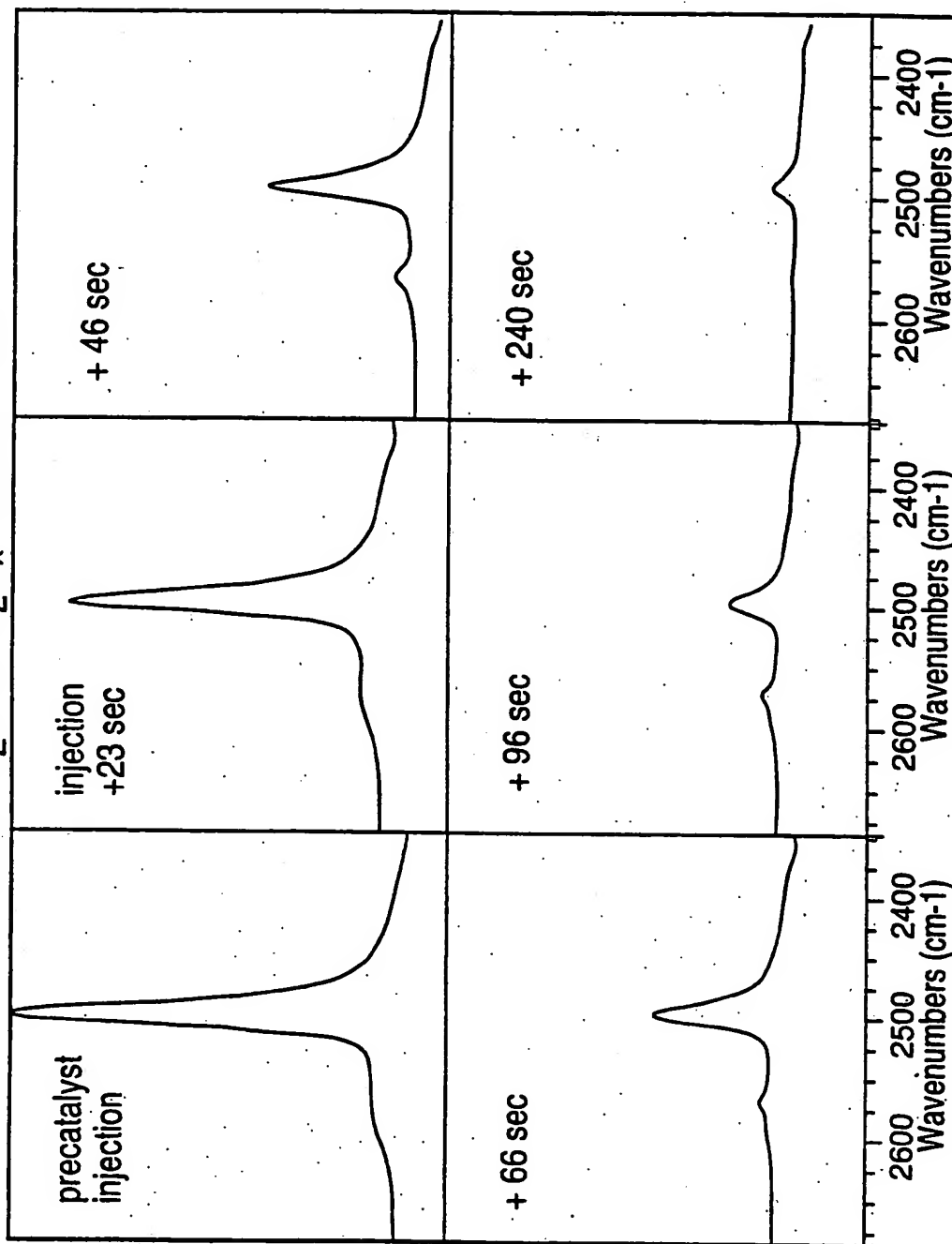History of H$_2$S and H$_2$S$_x$ Peaks of FIG.5.

FIG.6.

History of H_2S and H_2S_x Peaks Using the Pilot-scale Contactor

Initial Sample

H_2S
H_2S_x

Sample 70 seconds After Catalyst Addition

H_2S
H_2S_x

other volatiles

3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200
Wavenumbers (cm-1)

FIG.7.

Typical Spectra of Feed and Product Samples for a Steady-State Flowthrough Test

Feed Sample

flowrate = 41.1 TPH
sulphur temperature = 152° C.
catalyst concentration = 4.8 ppmw

H_2S_x

H_2S

Product Sample

70 % overall decrease
(2.5 min residence time)

H_2S_x

H_2S

other volatiles

3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200
Wavenumbers (cm-1)
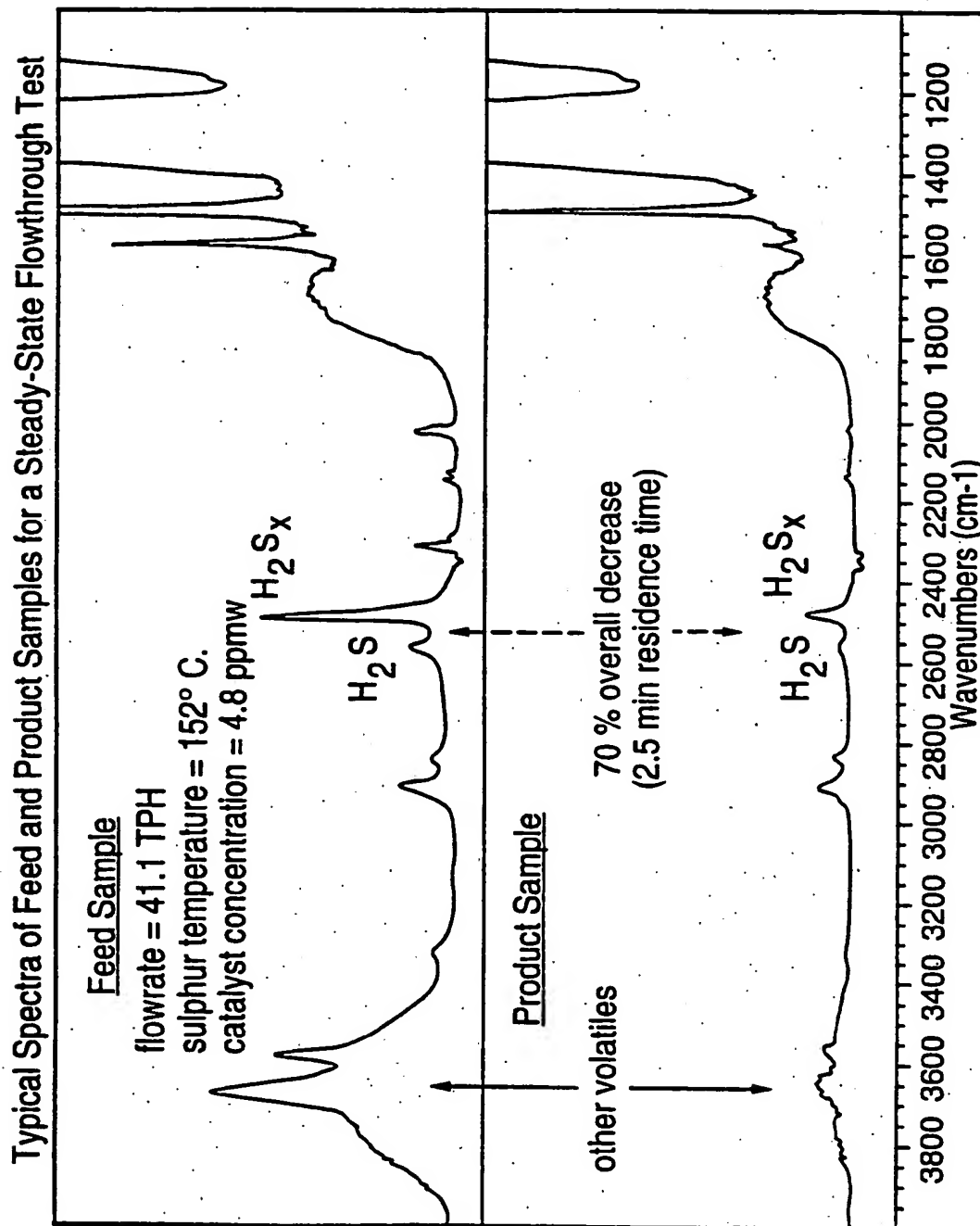
FIG.8.

H$_2$S$_x$ Half-life vs Catalyst Concentration
Pilot-scale Contactor, Continuous Flow Through Tests

FIG.9.

Spectra of Feed and Well Degassed Product

← Initial Feed
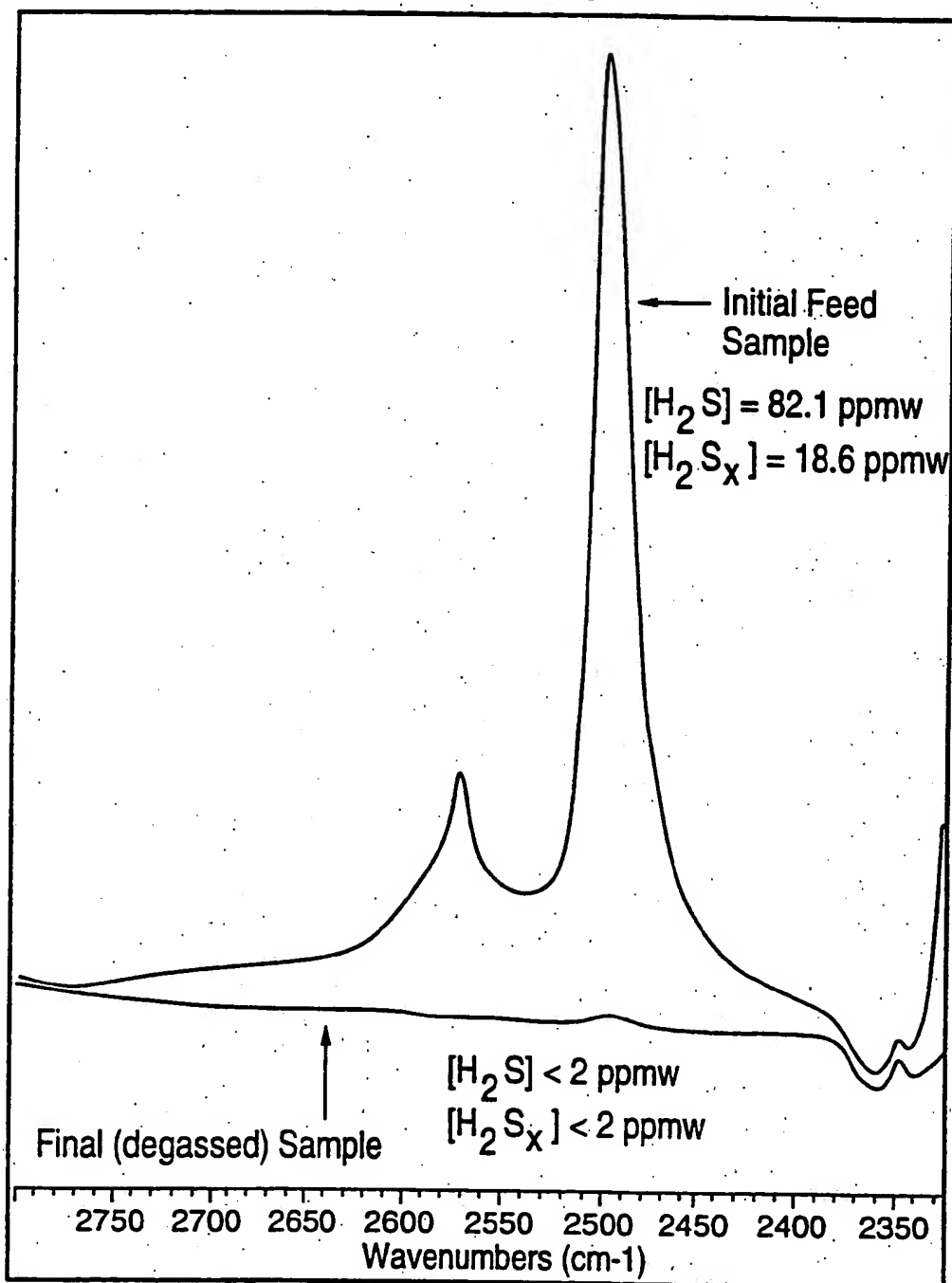Sample

$[H_2S] = 82.1$ ppmw

$[H_2S_x] = 18.6$ ppmw

Final (degassed) Sample

$[H_2S] < 2$ ppmw

$[H_2S_x] < 2$ ppmw

Wavenumbers (cm-1)

FIG.10.

FIG.11.

International application No.
PCT/CA 94/00481

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C01B17/02   C01B17/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 185 587 (SHELL) 4 January 1974 see the whole document ---	1-22, 54-65
A	EP,A,0 252 836 (SOC. NAT. ELF AQUIT.) 13 January 1988 see the whole document ---	1,2, 10-22, 54,58-65
A	WO,A,91 08038 (THE UNIVERSITY OF TORONTO) 13 June 1991 see the whole document & US,A,5 174 973 (SMITH ET AL.) cited in the application ---	1,23-33, 52,53, 66-68, 78,79

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 November 1994	15. 12. 94

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Zalm, W

Form PCT/ISA/210 (second sheet) (July 1992)

International application No.

PCT/CA 94/00481

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 116, no. 2, January 1992, Columbus, Ohio, US; abstract no. 8466r, H.J. KLOCKOW ET AL. 'Apparatus for removing residual gas from molten sulfur.' page 107 ; see abstract & DD,A,292 635 (INGENIEURBETRIEB ANLAGENBAU LEIPZIG)) 8 August 1991	1,23-33, 52,53, 66-68, 78,79
A	FR,A,1 336 701 (ELLIOTT) 1963 see the whole document	1,23-33, 52,53, 66-68, 78,79
A	CHEMICAL ABSTRACTS, vol. 101, no. 14, October 1984, Columbus, Ohio, US; abstract no. 113219a, F.R. ISMAGILOV ET AL. 'Removal of hydrogen sulfide from liquid sulfur.' page 123 ; see abstract & SU,A,1 104 105 (VOLGA-URAL SCIENT. RES INST.) 23 July 1984	3,9
A	EP,A,0 030 447 (HUDSON'S BAY OIL AND GAS COMPANY) 17 June 1981 see the whole document	54,58
T	SULPHUR, vol.233, no.4, August 1994, LONDON (GB) pages 35 - 45 'Controlling H2S evolution from sulphur.' see page 43, column 2, last paragraph - page 44, column 1	1-80

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2185587	04-01-74	BE-A-	799523	16-11-73
		CA-A-	1002730	04-01-77
		DE-A,C	2326058	13-12-73
		GB-A-	1433822	28-04-76
		NL-A-	7206948	27-11-73
EP-A-0252836	13-01-88	FR-A-	2601350	15-01-88
		AU-B-	602711	25-10-90
		AU-A-	7696587	10-02-88
		DK-B-	168283	07-03-94
		WO-A-	8800571	28-01-88
		JP-T-	1500588	01-03-89
		SU-A-	1634131	07-03-91
		US-A-	4849204	18-07-89
		US-A-	5030438	09-07-91
WO-A-9108038	13-06-91	CA-A-	2004652	05-06-91
		AU-B-	636495	29-04-93
		AU-A-	7895491	26-06-91
		CA-A-	2070630	06-06-91
		DE-D-	69004578	16-12-93
		DE-T-	69004578	05-05-94
		EP-A-	0504203	23-09-92
		ES-T-	2048007	01-03-94
		JP-B-	6077664	05-10-94
		JP-T-	5500632	12-02-93
		US-A-	5174973	29-12-92
		US-A-	5352421	04-10-94
US-A-5174973	29-12-92	CA-A-	2004652	05-06-91
		AU-B-	636495	29-04-93
		AU-A-	7895491	26-06-91
		CA-A-	2070630	06-06-91
		WO-A-	9108038	13-06-91
		DE-D-	69004578	16-12-93
		DE-T-	69004578	05-05-94
		EP-A-	0504203	23-09-92
		ES-T-	2048007	01-03-94
		JP-B-	6077664	05-10-94
		JP-T-	5500632	12-02-93

Form PCT/ISA/210 (patent family annex) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5174973		US-A-	5352421	04-10-94
DD-A-292635		NONE		
FR-A-1336701		NONE		
SU-A-1104105	23-07-84	NONE		
EP-A-0030447	17-06-81	CA-A-	1142326	08-03-83
		JP-A-	56155004	01-12-81
		US-A-	4280990	28-07-81

Form PCT/ISA/210 (patent family annex) (July 1992)